THE VAPOR COMPOSITION IN THE HALIDE SYSTEMS OF CERTAIN ALKALI AND ALKALI EARTH METALS

G.I. Novikov, A.L. Kuz'menko

Translation of "O sostave para v sistemakh galogenidov nekotorykh
shchelochnykh i shchelochnozemel'nykh metallov."
Vestnik Leningradskogo Universiteta, Seriya
Fizicheskaya i Khimicheskaya. No. 16, pp 143-149, 1964.

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
WASHINGTON, D.C.   JUNE 1966

THE VAPOR COMPOSITION IN THE HALIDE SYSTEMS OF CERTAIN ALKALI AND ALKALI EARTH METALS

G.I. Novikov, A.L. Kuz'menko

33721

ABSTRACT

Using our previously published data on vapour pressure and condensate analysis in the $KCl-CaCl_2$ and $KCL-SrCl_2$ systems, vapour composition ($KMeCl_3$ – form taken into consideration) and equilibrium rate constants of the dissociation process of this compound in the vapour phase and its thermodynamical characteristis have been determined. According to data in the literature, the thermodynamical dissociation characteristics of some binary compounds in the vapour phase has been determined.

When studying the vapor composition in the halide systems of alkali /143* metals with the halides of other elements in the periodic system, the authors of (Ref. 1-13) discovered numerous facts regarding the conversion of binary or acid complex types of compounds into vapor. The nature of these compounds has not yet been discovered.

The ability of these compounds to change into vapor has been studied most extensively for elements in the three-valent state [Al^{+3} (Ref. 1-5), Fe^{+3} (Ref. 6), and lanthanides (Ref. 7-9)], although there are similar data for elements in the 2- and 4-valent states. A determination has been made of the

---

* Note: Numbers in the margin indicate pagination in the original foreign text.

volatility of binary compounds in the KCl-FeCl$_2$ (Ref. 6), KCl-PbCl$_2$ and

KCl-CdCl$_2$ (Ref. 10), NaCl-BeCl$_2$ and KCL-BeCl$_2$ (Ref. 11), NaF-BeF$_2$ (Ref. 12)

MF-ZrF$_4$ (M=Li, Na, Rb) (Ref. 13, 14) systems.

However, researchers have very rarely had an adequate amount of experi-
mental data at their disposal to perform an accurate computation of the

equilibrium constants and the thermodynamic characteristics. Therefore, only

individual works have performed these computations, which makes it difficult to

systematize the existing material.

This article attempts to clarify certain thermodynamic characteristics of

vaporous binary compounds in the chloride systems of alkali and alkali earth

elements, based on our data and data presented in the literature. The experi-
mental data which were lacking has been augmented by approximate computations.

In our preceding report (Ref. 15), data were presented on the vapor pres-
sure and the over-all composition of sublimates in KCl-CaCl$_2$ and KCl-SrCl$_2$

systems. The conclusion was reached that it was impossible to explain the re-
sults obtained without assuming that molecules of the binary compounds were

changed into vapor. Under the condition that the forms of the vaporous mole-
cules were known, the data presented in this study made it possible to determine

the vapor composition by employing a method presented in (Ref. 16). However,

the great difference in the chloride vapor pressure of alkali and alkali earth

metals makes it impossible to determine the partial pressure of calcium

chloride or strontium chloride by solving the corresponding systems of equa-
tions concurrently. Therefore, we were compelled to calculate the pressures of

these forms approximately, by employing Raoult's law.

$$P_{MCl_2} = P^0_{MCl_2} \cdot \bar{x},$$

2

where $\bar{x}$ is the over-all molar portion of MCl_2 in the melt.

By analogy with the forms of vaporous dimers of alkali metal chlorides, it may be assumed that $KMCl_3$ is most probably the form of binary compounds <u>/144</u> in vapors. The partial pressures for each of them, as well as for KCl and K_2Cl_2, were computed from the experimental data by solving the corresponding systems of equations. Thus, with allowance for the $KMCl_3$ form and disregarding the small quantity P_{MCl_2}, this system assumes the final form:

$$P_{tot} = P_{KCl} + P_{K_2Cl_2} + P_{KMCl_3},$$
$$N = \frac{P_{KMCl_3}}{P_{KCl} + 2P_{K_2Cl_2} + P_{KMCl_3}},$$
$$K_p = \frac{P_{KCl}^2}{P_{K_2Cl_2}},$$

where N is the ratio between the number of moles of MCl_2 and KCl in the condensate, and the above equation represents the equilibrium constant of $(K_2Cl_2) = 2(KCl)$, the value for which was taken from (Ref. 17) for different temperatures.

The concurrent solution of these equations leads to the following expressions for the partial pressures of KCl and $KMCl_3$:

$$P_{KCl} = \frac{\left[\sqrt{(N+1)^2 + \frac{4P_{tot}}{K_p}(2N+1)} - (N+1) \right] K_p}{2(2N+1)}$$
$$P_{KMCl_3} = \frac{(2P_{tot} - P_{KCl}) N}{2N+1}.$$

Table 1 presents the computational results for the $KCl-CaCl_2$ and $KCl-SrCl_2$ systems. The partial pressures computed in this way for the individual vapor components enables us to compute the equilibrium constants of $(KMCl_3) = (KCl) + (MCl_2)$ for 1050 and 1150°C, which are given in Tables 2 and 3.

3

TABLE 1

VAPOR COMPOSITION IN $CaCl_2$-KCl and $SrCl_2$-KCl SYSTEMS WITH ALLOWANCE
FOR THE FORMATION OF $KMCl_3$ FORM

$T°C$	Melt Comp. (Mole %)	$P_{tot}·10^2$ ab. atm.	$P_{KCl}·10^2$ ab. atm.	$P_{K_2Cl_2}·10^2$ ab. atm.	$P_{KMCl_3}·10^2$ ab. atm.	$P_{MCl_2}·10^4$ ab. atm.
			KCl-$CaCl_2$			
1050	25	0.53	0.34	0.01	0.18	0.69
1050	50	1.18	0.84	0.05	0.28	0.46
1050	75	2.63	2.00	0.30	0.33	0.23
1150	25	1.58	1.02	0.03	0.54	3.75
1150	50	3.68	2.65	0.17	0.86	2.50
1150	75	6.32	4.93	0.60	0.80	1.25
			KCl-$SrCl_2$			
1050	25	0.79	0.60	0.03	0.17	0.20
1050	50	1.45	1.16	0.10	0.19	0.13
1050	75	2.76	2.26	0.38	0.12	0.07
1150	25	1.97	1.50	0.06	0.42	1.19
1150	50	4.41	3.51	0.31	0.58	0.78
1150	75	7.24	6.02	0.90	0.31	0.40

It can be seen from Table 2 that the values of K_p (in the case of T = const) change very slightly during the conversion from one melt composition to another; based on this fact, we may conclude that the form $KMCl_3$ was selected correctly. The position for the maxima of the partial pressure of $KCaCl_3$ and $KSrCl_3$ also indicates this (Table 1).

The values of K_p for the dissociation equilibrium of $KMCl_3$ from Table 2, as well as their mean values from Table 3, were employed to compute the thermodynamic characteristics:

$$(KCaCl_3) = (KCl) + (CaCl_2),$$
$$\Delta H^°_{1373°K} = 63 \pm 3 \text{ kcal/mole}, \quad \Delta S^°_{1373°K} = 30 \pm 2 \quad \text{units of energy}$$
$$(KSrCl_3) = (KCl) + (SrCl_2),$$
$$\Delta H^°_{1373°K} = 67 \pm 17 \text{ kcal/mole} \quad \Delta S^°_{1373°K} = 32 \pm 13 \text{ units of energy}$$

TABLE 2 /145

EQUILIBRIUM CONSTANTS (K_p)

$T°C$	Melt Comp. (Mole%KCl)	$(KCaCl_3)=(KCl)+(CaCl_2)$	$(KSrCl_3)=(KCl)+(SrCl_2)$
1050	25	$1,31 \cdot 10^{-4}$	$0,69 \cdot 10^{-4}$
1050	50	1,38	0,81
1050	75	1,39	1,24
1150	25	$7,08 \cdot 10^{-4}$	$4,45 \cdot 10^{-4}$
1150	50	7,71	4,78
1150	75	7,71	7,67

TABLE 3

MEAN VALUES OF K_p and $\lg K_p$

$T°C$		$(KCaCl_3)=(KCl)+(CaCl_2)$	$(KSrCl_3)=(KCl)+(SrCl_2)$
1050	K_p	$(1,36 \pm 0,04) \cdot 10^{-4}$	$(0,92 \pm 0,29) \cdot 10^{-4}$
	$\lg K_p$	$-3,867 \pm 0,012$	$-4,053 \pm 0,100$
1150	K_p	$(7,50 \pm 0,28) \cdot 10^{-4}$	$(5,63 \pm 1,36) \cdot 10^{-4}$
	$\lg K_p$	$-3,125 \pm 0,016$	$-3,263 \pm 0,100$

The values of $H_T^°$ and $\Delta S_T^°$ thus obtained for both equilibriums were very close to each other, which would be naturally expected for such similar systems and processes. The values of $\Delta H_T^°$ and $S_T^°$ which are close to the corresponding characteristics in the $KCl-LnCl_3$ systems are also very probable (Ref. 6-8).

It would be interesting to compare the computational data presented above for the $KCl-CaCl_2$ and $KCl-SrCl_2$ systems with certain data presented in the literature for similar systems of two elements in the II group of the periodic system. The data presented by Sheyko andFeshchenko (Ref. 11) would be most interesting from this point of view. Although the authors conclude that binary compounds are present in the vapors, they do not compute the vapor composition or the equilibrium characteristics due to the lack of data with which

to find accurate values. However, an approximate solution of the problem, similar to that presented above, is possible. This possibility lies in the fact that the experimental data in (Ref. 11) pertain to temperatures which do not exceed 600°C, and to pressures ranging from 2 mm Hg to several hundreds. In view of this fact, the partial pressures of simple forms of alkali metal chlorides may be disregarded during the computation, as was done in the cases presented above.

It may be seen from the literature that beryllium chloride is par- tially dimerized in vapors (Ref. 18, 19), and the following equilibrium characteristic of $(Be_2Cl_4) = 2(BeCl_2)$ is presented:

$$\lg K_p = 9.84 - \frac{8030}{T°K}.$$

By employing this equation, we may readily show that the pressure of the dimeric form of vapor may also be disregarded in the 300-600°C range.

On the basis of the data in (Ref. 11), we have computed the over-all composition of the vapor (N), as presented in Table 4. It may be seen from this table that, in spite of the low temperatures and high pressures of the vapor, as well as the great difference in volatility of the simple forms, the vapor in the KCl-BeCl$_2$ system contains comparable amounts of these forms. This fact comprises the main verification of the existence of binary compounds in vapors.

The partial pressures of BeCl$_2$ and the binary compound MBeCl$_3$ were computed from data on the total vapor pressure and the over-all composition of sublimates upon the melts, with allowance for the assumptions formulated above according to the equations

$$P_{tot} = P_{BeCl_2} + P_{MBeCl_3},$$

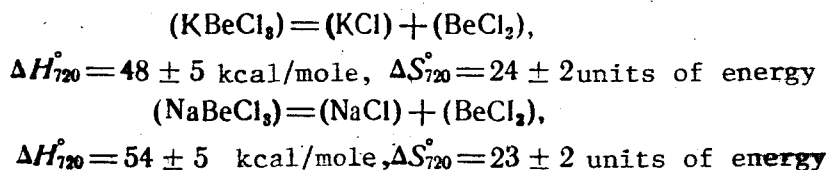$$N = \frac{P_{MBeCl_3}}{P_{BeCl_2} + P_{MBeCl_3}}.$$

TABLE 4

OVER-ALL VAPOR COMPOSITION IN MCl-BeCl$_2$ SYSTEMS

Melt Comp. (Mole % MCl)	Temperature Range (°C)	$N = \dfrac{P'_{MCl}}{P_{BeCl_2}}$
NaCl—BeCl$_2$		
49	300—590	0,01
60	350—600	0,3
70	580—590	0,8
KCl—BeCl$_2$		
35	300—570	0,11
51	300—600	0,03

The values for the partial pressures of MCl(M = K, N$_a$) which are lacking

in these equations, were determined by Raoult's law from the pressure of the

saturated vapor for the compounds at the corresponding temperatures, with allow-

ance for partial dimerization in the vapors (Ref. 20).

The equilibrium constants which we computed at different temperatures were

employed to determine the thermodynamic equilibrium characteristics:

$$(KBeCl_3) = (KCl) + (BeCl_2),$$
$$\Delta H^{\circ}_{720} = 48 \pm 5 \text{ kcal/mole}, \quad \Delta S^{\circ}_{720} = 24 \pm 2 \text{units of energy}$$
$$(NaBeCl_3) = (NaCl) + (BeCl_2),$$
$$\Delta H^{\circ}_{720} = 54 \pm 5 \text{ kcal/mole}, \Delta S^{\circ}_{720} = 23 \pm 2 \text{ units of energy}$$

The material presented in the work by Schries and Clark (Ref. 22)

for the KCl-MgCl$_2$ system is extremely interesting. By analyzing the data ob-

tained by the boiling point and gas saturation methods, the authors of this

article established the conversion of the KMgCl$_3$ compound into vapor, and com-

puted the vapor composition. Unfortunately, they have presented practically no

numerical computations, and we were thus able to employ only limited data on

vapor composition at 1075°C, which are given in Table 5.

TABLE 5

VAPOR COMPOSITION IN THE KCl-MgCl$_2$ SYSTEM AT 1075°C

Melt Composition (Mole %)	P_{KCl} (mm Hg)	P_{MgCl_2} (mm Hg)	$P_{Mg_2Cl_4}$ (mm Hg)	P_{KMgCl_3} (mm Hg)	$Kp = \dfrac{P_{KCl} \cdot P_{MGCl_2}}{P_{KMgCl_3}}$
20	0.7	23.0	8	4.5	$4.72 \cdot 10^{-4}$
40	2.0	10.5	2	15.0	$18.4 \cdot 10^{-4}$
60	6.5	4.5	–	14.0	$27.5 \cdot 10^{-4}$
80	18.5	1.5	–	4.0	$91.5 \cdot 10^{-4}$

It can be seen from the table that the values of K_p depend greatly on the melt composition, which points either to the prior accuracy of the experimental data, or to the necessity of allowing for certain vapor components.

Since the data presented in Table 5 pertain to one single temperature, they may be used to calculate only the value $\Delta F^o_{1348°K}$, which is obtained as 16.5 ± 2.3 kcal/mole.

By analogy with the monotypic equilibriums presented above, with allowance for the location of magnesium among the other alkali earth metals, for the equilibrium of $(KMgCl_2) = (KCl) + (MgCl_2)$ we may assume a value of $\Delta S^o_{1348°K}$ which equals 31 units of energy; thus, $\Delta H^o_{1348°K}$ of the process will be 58 ± 5 kcal/mole.

In addition to systems formed by the chlorides of alkali and alkali earth elements, it is interesting to examine the following experimental data for the NaF – BeF$_2$ system, and to compare the data presented above for the NaCl – BeCl$_2$ system with them.

In a study devoted to studying the N$_{aF}$ – BeF$_2$ system, Sense and Stone (Ref. 12) show that in this case the vapor also contains the binary compound

NaBeF$_3$ in addition to simple forms. The authors do not present the thermo-

dynamic characteristics of this compound. By employing the experimental data

in this work, we made an approximate calculation of certain thermodynamic

characteristics for the dissociation process of a binary compound in the vapor

phase. The information necessary for this on the vapor composition was ob-

tained, based on the following assumptions:

1. Due to the fact that the equilibrium (Be$_2$F$_4$) = 2(BeF$_2$) could not be in-

vestigated, by comparing the data on Be$_2$Cl$_4$ (Ref. 17, 18), Mg$_2$Cl$_4$ (Ref. 21),

and Mg$_2$F$_4$ (Ref. 22) we determined the values of the constants A and B in the

equation lg K$_p$ = A $-$ $\frac{B}{T}$ for this process. These values equaled 12.67 and 15730,

respectively. Thus, the vapor of BeF$_2$ must contain 90-95% monomer for the

800 - 1000°C range. Therefore, we did not take into account the form of

Be$_2$F$_4$ in the vapors in our approximate computations.

2. The partial pressures of BeF$_2$ and of the binary compound, dis-   <u>/148</u>

regarding the pressure of NaF as a small quantity, were computed in the

50 - 100 mole %   BeF$_2$ range.

3. The partial pressure of NaF was computed approximately, by employing

Raoult's law as well as data on the saturated vapor of a monomer (Ref. 20).

Since the total vapor pressure is not given in (Ref. 12), but only the par-

tial pressure of P$'_{BeF_2}$ and P$_{NaF}$, calculated without allowance for the forma-

tion of a binary compound in the vapors, the equation requisite for computing

the vapor composition in the form NaBeF$_3$ has the following form:

$$(P'_{BeF_2} + P'_{NaF}) = P_{BeF_2} + 2P_{NaBeF_3}$$

9

The second equation is

$$N = \frac{P_{BeF_2} + P_{NaBeF_3}}{P_{NaBeF_3}}.$$

The results derived from calculating the vapor composition show that the values which we calculated for the partial pressures of the binary form as a function of the over-all melt composition passed through a maximum close to 50 mole % NaF, which corresponds to the form $NaBeF_3$ and coincides with the conclusion formulated in (Ref. 12). By employing the data thus obtained on the vapor composition, we were able to compute the equilibrium constants of the dissociation process in $NaBeF_3$ vapors.

Assuming that the data pertaining to melts containing 26.1 and 41.2 mole % NaF are more accurate, we employed them to compute the thermodynamic equilibrium characteristics:

$$(NaBeF_3) = (NaF + BeF_2),$$
$$\Delta H^{\circ}_{1180^{\circ}K} = 52 \pm 2 \text{ kcal/mole}, \quad \Delta S^{\circ}_{1180^{\circ}K} = 21 \pm \text{ units of energy}$$

The data presented do not exhaust the existing information on the formation of halide binary compounds of elements in groups I and II of the periodic system in vapors. As has already been indicated, the conclusion was reached in (Ref. 10) that a binary compound with an unknown composition exists in the vaporous phase of the $KCl - CdCl_2$ system. Unfortunately, the authors of this article present no quantitative data which would facilitate the computations.

REFERENCES

1. Porter, F., Zeller, E. J. chem. phys. 33, 858, 1960.

2. Morozov, I. S., Toptygin, D. Ya. Zhurnal Neorganicheskoy Khimii, 3, 1637, 1958.

3. Howard, E. J. Amer. chem. soc., 76, 2041, 1954.

4. Dewing, E. J. Amer. chem. soc., 77, 2639, 1955.

5. Vetyukov, M. M. et al. Izvestiya Vysshikh Uchebnykh Zavendeniy, No. 6, 126, 1959.

6. Grote, H. Zs. Elecktrochem., 54 (3), 216, 1950.

7. Novikov, G. N., Bayev, A. K. Zhurnal Obshchey Khimii, 32, 315, 1962.

8. Idem. Vesntik Leningradskogo Universiteta, No. 16, 89, 1962.

9. Idem. Zhurnal Neorganicheskoy Khimii, 7, 1353, 1962.

10. Barton, I., Bloom, H. Trans. Farad. soc., 55, 1792, 1959.

11. Sheyko, N., Feshchenko, V. G. Ukrainskiy Khimicheskiy Zhurnal, 28, 478, 1962.

12. Sense, K., Stone, R. J. phys. chem., 61, 337, 1957.

13. Sense, K. et. al. J. Phys..chem., 61, 337, 1957.

14. Sense, K., Stone, R. J. phys. chem..62, 1411, 1958.

15. Frid, S. A., Polyachenok, O.G., Novikov, G. I. Zhurnal Neorganicheskoy Khimii, 9, 1017, 1964.

16. Novikov, G. I., Bayev, A. K. Zhurnal Neorganicheskoy Khimii, 9, 1672, 1964.

17. Datz, S., Smith, W., Taylor. J. chem. phys., 34, 558, 1961.

18. Ralfs, O., Fischer, W. Zs. anorg. u. allg. Chem., 211, 349, 1933.

19. Ryabchikov, L. N., Tikhinskiy, G. F. Fizika Metallov i Metallovedeniye, 10, 635, 1960.

21. Gurvich, L. V., et al. Thermodynamic Properties of Individual Substances (Termodinamich. svoystva individual'nykh veshchestv), II, Izdatel'stvo AN SSSR, Moscow, 1962.

22. Milne, T. Cubbicciotti, D. J. chem. phys., 29, 846, 1958.

23. Schries, E., Clark, H. J. phys. chem. 67, 1259, 1963.